PHYSICAL REVIEW B VOLUME 28, NUMBER 11 1 DECEMBER 1983

Relativistic spin polarization and magnetization: Knight shift of Pt(001)

M. Weinert
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

A. J. Freeman
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

(Received 22 July 1983)

A relativistic local-density approach for including magnetic effects into scalar-relativistic electronic structure methods is presented. This method is based on a spin-only relativistic generalization of density-functional theory and on results for the relativistic homogeneous electron gas. The relativistic effects on the magnetization density are found to be important only near the nucleus and hence to affect Fermi-contact hyperfine interactions. The approach is illustrated by means of a detailed determination of the Knight shift K of a thin Pt(001) film. These results show a large positive change in K at the surface with respect to the bulk due to a decreased magnetization at the surface (and hence a decrease in the magnitude of the negative core polarization) plus an increased positive valence-electron contribution. The spin-only value of K in the surface layer is -0.6% versus a center-layer value of -4.1% (compared with the experimental bulk value of -3.4%, which includes a positive orbital contribution). The core polarization per unpaired spin (-1.1×10^6 Oe/μ_B) is in excellent agreement with experiment (-1.2×10^6 Oe/μ_B). These results give both a qualitative and quantitative understanding of recent NMR experiments on small Pt particles.

I. INTRODUCTION

One of the goals of surface science is to understand catalysis from a microscopic point of view. One of the most important catalysts (and hence of particular interest) is Pt, usually in the form of small particles. Recently, several NMR studies on superfine Pt particles[1-6] have been reported with emphasis on the surface properties. Pt is a good candidate for NMR since the ^{195}Pt nucleus is 34 at. % abundant, of spin $\frac{1}{2}$, and has one of the largest Knight shifts of any metal (-3.37%).[7] The Knight shift K is defined[8] as the relative shift in the NMR frequency ω_0 of a nucleus (with gyromagnetic ratio γ) in a dc magnetic field H_0 due to the polarization of the conduction electrons in a metal,

$$\omega_0=\gamma(1+K)H_0 ,$$

where the frequency of the bare nucleus is just γH_0. The main contributions to the Knight shift arise from the orbital paramagnetism and the Fermi-contact terms due to the valence electrons and core polarization.

The results of Yu *et al.*[1,2] on particles $\lesssim 200$ Å in diameter showed a broadening of the resonance line that varied inversely with particle size. The experiments by Slichter *et al.*[3-6] on smaller particles with diameters in the range 10—100 Å showed a distribution of the NMR signal ranging from the bulk signal to positive values of K. The sharp peaks for which $K>0$ were attributed to the adsorption of gas molecules[4,5] on the surface of the particles. If the particles are then cleaned, these sharp peaks disappear, but a rather broad peak at $K\approx0\%$ still remains.[4,5] This broad peak can then be identified with the clean surface.

In order to obtain a microscopic understanding of these results, it is necessary to understand the electronic and magnetic structure of the bulk and surface in the presence of an external field. An important conceptual problem that arises in the straightforward application of the standard (spin-) density-functional (SDF) theory[9,10] to this problem for heavy materials such as Pt is that spin and kinetic effects are not separable in a relativistic treatment. The relativistic generalization[11] of the SDF theory handles this problem by considering the external fields as given classical objects within a spin-only framework. In Sec. II we present a practical local-density approximation which includes relativistic corrections to the spin density in the spirit of the local-spin-density method (LSD).[10] While based on the relativistic generalization of density-functional (DF) theory,[11] our approach has the conceptual appeal of showing the transition between the relativistic and nonrelativistic limits. This procedure as implemented into the full-potential linearized augmented-plane-wave (FLAPW) method[12] for thin films and applied to the case of a thin Pt(001) film is described in Sec. III. In Sec. IV we present the theoretical spin-orbit Knight shifts.[13] The results using the relativistic spin-polarized approach described in Sec. II give both a qualitative and quantitative description of the experimental trends,[4,5] thereby leading to a microscopic understanding of the data. Finally in Sec. V we give some further discussion and summarize the main results.

II. THEORY OF RELATIVISTIC SPIN POLARIZATION

Consider the coupling of Dirac particles of mass m and charge e to the electromagnetic field (we will be in the radiation gauge $\nabla\cdot A=0$).[14] We write

$$\hat{\mathscr{H}}=\hat{\mathscr{H}}_0+\frac{1}{c}\int d\vec{r}\,\hat{J}_\mu A^\mu \;, \tag{1}$$

where $\hat{\mathscr{H}}_0$ is the Hamiltonian in the absence of external fields and the four-current operator and four-potential are given by

$$\hat{J}^\mu=(c\hat{\rho},\hat{\vec{J}}\,)=ec\hat{\bar{\psi}}(\vec{r})\gamma^\mu\hat{\psi}(\vec{r}) \;, \tag{2}$$

$$A^\mu=(\Phi,\vec{A}_{\rm ext}) \;. \tag{3}$$

(Our notation follows the convention of Bjorken and Drell.[14]) Rajagopal and Callaway,[15] MacDonald and Vosko,[11] and Rajagopal[16] have shown that the Hohenberg-Kohn theorems[9] on which DF theory is based can be generalized to include relativistic effects. Moreover, these authors have shown that one can obtain Kohn-Sham single-particle equations of the form[11]

$$\{c\vec{\alpha}\cdot[\vec{p}-(e/c)\vec{A}_{\rm eff}]+\beta mc^2+eV_{\rm eff}(\vec{r})\}\phi_i(\vec{r})=\epsilon_i\phi_i(\vec{r}) \;, \tag{4}$$

where the effective potentials are given by

$$V_{\rm eff}(\vec{r})=\Phi(\vec{r})+e\int\frac{n(\vec{r}\,')d\vec{r}\,'}{|\vec{r}-\vec{r}\,'|}+\frac{\delta E_{\rm xc}[J_\mu]}{\delta J_0(\vec{r})} \;, \tag{5}$$

$$\vec{A}_{\rm eff}(\vec{r})=\vec{A}_{\rm ext}-\frac{\delta E_{\rm xc}[J_\mu]}{\delta J(\vec{r})} \;, \tag{6}$$

and $n(\vec{r})$ is the number density. The exchange-correlation energy functional $E_{\rm xc}[J_\mu]$ contains magnetic effects through its dependence on the spatial components of the current. If we are interested in spin effects, this approach is not appropriate since spin and kinetic effects are not separable. Following MacDonald and Vosko,[11] we take the nonrelativistic viewpoint that the external fields (in analogy with nonrelativistic SDF theory) couple only to the particle and spin densities,

$$\begin{aligned}\hat{\mathscr{H}}_{\rm ext}={}& e\int d\vec{r}:\hat{\bar{\psi}}(\vec{r})\gamma_0\hat{\psi}(\vec{r}):\Phi(\vec{r})\\ &-\frac{\mu_B}{2}\int d\vec{r}:\hat{\bar{\psi}}(\vec{r})\sigma_{\mu\nu}\hat{\psi}(\vec{r}):F^{\mu\nu}_{\rm ext}(\vec{r}) \;,\end{aligned} \tag{7}$$

where μ_B is the Bohr magneton and

$$\sigma^{\mu\nu}=\tfrac{1}{2}i[\gamma^\mu,\gamma^\nu] \;, \tag{8}$$

$$F^{\mu\nu}=\partial^\mu A^\mu-\partial^\nu A^\nu \;. \tag{9}$$

If we consider A^μ and $F^{\mu\nu}$ to be given classical objects with $F^{\mu\nu}$ having only spatial components, we have[11]

$$\begin{aligned}\hat{\mathscr{H}}_{\rm ext}={}& e\int d\vec{r}:\hat{\bar{\psi}}(\vec{r})\gamma_0\hat{\psi}(\vec{r}):\Phi(\vec{r})\\ &-\mu_B\int d\vec{r}[:\hat{\bar{\psi}}(\vec{r})\vec{\sigma}\hat{\psi}(\vec{r}):]\cdot\vec{B} \;.\end{aligned}$$

If we now define the magnetization density operator $\hat{\vec{m}}(\vec{r})=\mu_B\hat{\bar{\psi}}\vec{\sigma}\hat{\psi}$, we can write

$$\hat{\mathscr{H}}_{\rm ext}=\int d\vec{r}\{\hat{\rho}(\vec{r})\Phi(\vec{r})-[\hat{\vec{m}}(\vec{r})]\cdot\vec{B}\} \;. \tag{10}$$

The first term contains the usual minimal electromagnetic coupling while the second term represents a coupling to the magnetic dipole moment only. This Hamiltonian leads to single-particle equations of the form

$$[c\vec{\alpha}\cdot\vec{p}+\beta mc^2+eV_{\rm eff}(\vec{r})-\mu_B\vec{\Sigma}\cdot\vec{U}_{\rm eff}(\vec{r})]\phi_i(\vec{r})=\epsilon_i\phi_i(\vec{r}) \;, \tag{11}$$

where $V_{\rm eff}(r)$ is given by Eq. (5) and the spin-density operator $\vec{\Sigma}$ and effective magnetic potential are given by

$$\vec{\Sigma}=\begin{bmatrix}\vec{\sigma} & 0\\ 0 & -\vec{\sigma}\end{bmatrix} \;, \tag{12}$$

$$\vec{U}_{\rm eff}=\vec{B}+\frac{\delta E_{\rm xc}}{\delta\vec{m}(\vec{r})} \;, \tag{13}$$

where $\vec{\sigma}$ denotes the usual 2×2 Pauli spinors. The number density $n(\vec{r})$ and magnetization density $\vec{m}(\vec{r})$ are given by

$$\begin{aligned}n(\vec{r})&=\sum_i\phi_i^\dagger(\vec{r})\phi_i(\vec{r}) \;,\\ \vec{m}(\vec{r})&=\mu_B\sum_i[\phi_i^\dagger(\vec{r})\vec{\Sigma}\phi_i(\vec{r})] \;,\end{aligned} \tag{14}$$

where the sums are over all occupied (positive-energy) states.

If we take the nonrelativistic limit of (11) retaining the first relativistic correction, we obtain the familiar Pauli-type equation for a magnetic field coupling to the spins only,[17]

$$\begin{aligned}\Bigg[\left[\frac{p^2}{2m}-\frac{p^4}{8m^3c^2}\right]-\mu_B\vec{\sigma}\cdot\left[\vec{B}-\frac{1}{2mc}(\nabla V\times\vec{p})\right]\\ +\left[eV+\frac{\hbar^2e}{8m^2c^2}\nabla^2V\right]\Bigg]\Psi=(\epsilon-mc^2)\Psi \;.\end{aligned} \tag{15}$$

In this equation $\vec{B}$ and V are the effective magnetic fields and potentials which include the exchange-correlation effects.

The set of self-consistent equations (5) and (11)—(14), in principle, yields the correct charge and magnetization densities. Unfortunately, since the exact exchange-correlation functional is not known, we will use the well-known local-density approximation.[9] This approximation has been well tested and gives excellent agreement with experiments for ground-state properties such as equilibrium geometry and charge and spin densities. For metals such as Pt, relativistic corrections to the exchange[11,16] and spin-orbit coupling do affect the Fermi surface,[18] but the valence charge and spin densities are rather insensitive to these effects.[18] Hence, we will treat the valence electrons scalar relativistically,[19] i.e., including all kinematic relativistic effects except spin-orbit effects. In this way, we avoid the well-known problems associated with solving the Dirac equation self-consistently for complex systems with large unit cells such as those encountered in surface systems. For the core electrons, on the other hand, the spin-orbit term can have large effects (especially for p functions), and hence we treat the core fully relativistically.

We are now left with the question of how to include magnetic and spin effects. The nonrelativistic viewpoint implicit in the form of the coupling in Eq. (10) suggests treating these effects in an analogous way to the nonrelativistic (local-) SDF method, i.e., solving the standard spin-polarized equations but with the nonrelativistic single-particle operator replaced by the scalar relativistic one. This prescription is obviously not exact, but only true in a perturbational sense. However, since we know that for light systems the relativistic equations must reduce to the standard nonrelativistic results, there is justification for this approach. For the magnetic fields and Pt surfaces which we will consider, the magnetization fraction (magnetization density divided by charge density) in the high-density (relativistic) core region is of the order 10^{-8}—10^{-6}; hence a perturbational expansion in terms of this factor will converge quite rapidly. For the nonrelativistic regions of space, this procedure reduces correctly to the standard spin-polarized one.

Using this approach, we are left with the question of how to obtain the magnetization density, or equivalently, the magnetization fraction, from the spin-polarized single-particle equations. In the nonrelativistic limit we would define the relative magnetization ζ as

$$\zeta=\frac{|\vec{m}_{\mathrm{NR}}|}{n}=\frac{n_\uparrow-n_\downarrow}{n_\uparrow+n_\downarrow}\ , \tag{16}$$

where $n_\uparrow$ ($n_\downarrow$) is the number density of up (down) electrons and $n=n_\uparrow+n_\downarrow$. Ramana and Rajagopal[20] have considered the case of a relativistic spin-polarized electron gas and have obtained a relationship for the relativistic magnetization fraction ξ,

$$\xi=\frac{|\vec{m}|}{n}\ , \tag{17}$$

using ζ as a parameter,[20]

$$\begin{aligned}\xi(\zeta)=\tfrac{1}{3}\zeta+\frac{1}{2\beta^3}\{&\beta x(1+\beta^2x^2)^{1/2}-\beta y(1+\beta^2y^2)^{1/2}\\&+\ln[\beta x+(1+\beta^2x^2)^{1/2}]\\&-\ln[\beta y+(1+\beta^2y^2)^{1/2}]\}\ ,\end{aligned} \tag{18}$$

where $x=(1+\zeta)^{1/3}$, $y=(1-\zeta)^{1/3}$, and

$$\beta=\hbar k_F/mc=\alpha(3\pi^2 n)^{1/3}$$

is a dimensionless relativistic expansion parameter depending on the density n. In the nonrelativistic case ($\beta\to 0$) the ratio ξ/ζ approaches one, while in the extreme relativistic limit ($\beta\to\infty$) the ratio approaches 1/3. This reduction of the relativistic magnetization fraction compared to the nonrelativistic case can be understood by noting[20] that helicity, and not spin, is a good quantum number; hence, each electron has both a "spin-up" and "spin-down" part. Note that this result implies that it is impossible to have a fully polarized relativistic electron gas. Likewise, if we have an external magnetic field, the spin-quantization axis of an electron in its rest frame is not parallel to the external field.

We will use Eq. (18) locally to transform the spin densities obtained from the scalar relativistic equations into the relativistic magnetization densities. This relativistic correction in Pt is important only very near the nucleus where it yields a factor of approximately half, while already for distances of the order of 0.5 bohr, the correction is less than 1%.

III. IMPLEMENTATION OF THE RELATIVISTIC APPROACH

Up to this point the discussion has been rather general; we now give a few more calculational details for our specific example of an ideal (unreconstructed) five-layer Pt(001) film with lattice constant $a=3.923$ Å. We solve our modified local- (spin-) density equations using the FLAPW method.[12] In this method, none of the standard shape approximations to the potential (such as muffin-tin, or overlapping, spherical densities) that would be suspect at a surface are made. This combined with the good variational freedom of the plane-wave-based basis set yields accurate solutions to the LSD equations. As discussed above, the spherical cores are treated fully relativistically, while the valence electrons are treated scalar relativistically. The local exchange-correlation potential of Hedin and Lundqvist[21] (with and without the relativistic corrections to exchange[11,16]) for the paramagnetic part and the spin-dependent potential of von Barth—Hedin[10] are used. The external magnetic field is included self-consistently as described earlier. In order to ensure that the density and magnetization densities are converged with respect to Brillouin-zone sampling, we have used 45 equally spaced k points in the irreducible two-dimensional (2D) wedge and a linear triangular integration scheme[22]; we have verified that the magnetization density at the nucleus is converged with respect to k points.

IV. RESULTS

Before considering the magnetic effects at the surface of Pt, we consider the electronic properties. The first question to address is whether a film of only five layers can reproduce both the bulk and surface properties. For metals, the screening lengths are of the order of interatomic spacings; hence, we expect our film to be thick enough. In Fig. 1 we present the charge density in a (110) plane perpendicular to the surface. As expected, the charge density is already bulklike at the subsurface layer. The local density of states (DOS) in each layer, shown in Fig. 2, further supports this contention: The central layer already has the characteristic bulk Pt DOS.[18] These results are consistent with the NMR spin-echo field-gradient results of Yu and Halperin[2] that the characteristic surface region has a thickness of 1.5±0.5 lattice constants independent of the size of the particles.

The work function, which depends on both bulk and surface properties, is another quantity of interest, especially since it gives some measure of the quality of the charge density in the surface region. In general, the agreement between theory and experiment is found to be on the order of a few tenths of an electron volt. Hence at first glance, the discrepancy between our calculated work function of

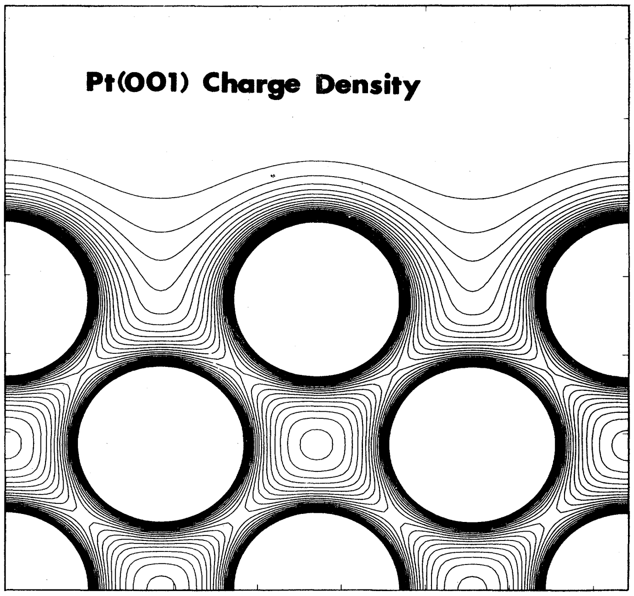

FIG. 1. Valence charge density in a (110) plane. Contour step size is 0.004 e/a.u.^{3} with a cutoff of 0.1 e/a.u.^{3}.

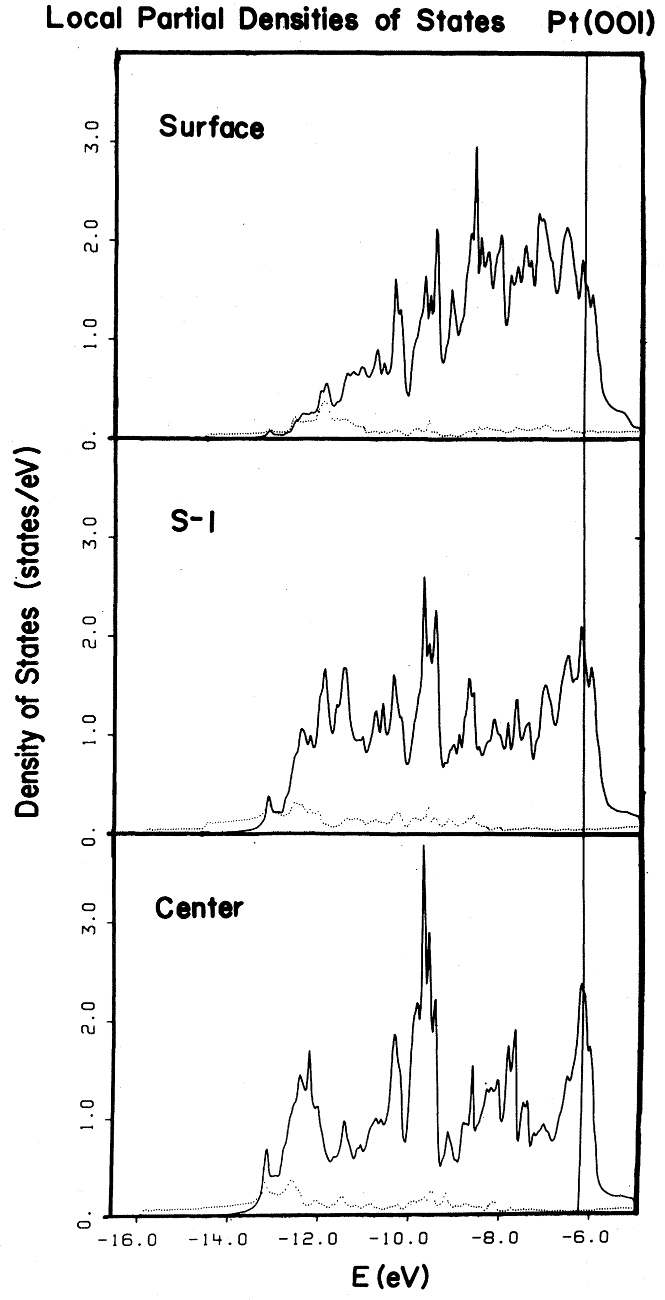

FIG. 2. Local partial DOS for paramagnetic Pt(001) five-layer film. Solid lines (dotted line) correspond to the d ($s+p$) DOS broadened by a Gaussian of 0.05 eV full width at half maximum.

6.2 eV and the experimental value of 5.84 eV for the Pt(001) surface[23] is rather disturbing. However, this experimental value of 5.84 eV was obtained in a field-emission experiment. Since in field-emission experiments the face-dependent work functions are determined relative to the total work function of the tip, it is necessary to either measure or assume a value of the total work function. Nieuwenhuys and Sachlter[23] assumed a value of 5.32 eV and suggest that this value is rather arbitrary. Other measurements on polycrystalline samples yield total work functions of 5.6–5.7 eV,[24] which suggest a shift of the field-emission values to larger work functions. This experimental uncertainty in the work function, coupled with the known 5×20 reconstruction of the Pt(001) surface suggests that our calculated work function is in quite good agreement with experiment.

At this point we should comment on our choice of a Pt(001) unreconstructed film as opposed to the actual 5×20 surface.[25] A major reason is purely computational: Although there are several models of the 5×20 surface, a high-quality calculation of this size is impractical because of the enormous size of the unit cell. More importantly, however, is the fact that the NMR experiments[1–6] that we wish to understand are on small particles. Since the features in the NMR spectra are similar for particles with widely varying dispersions (and distributions of crystal faces and sizes), it appears that the effects are not highly face dependent. Hence, by studying an idealized, but well-defined model that describes both bulk- and surface-like properties, we hope to be able to extract trends and obtain at least semiquantitative agreement with experiment.

The Pt films studied here are nonmagnetic in the absence of an external applied field. From theoretical studies[18] of the bulk, Pt is found to be a Stoner-type paramagnet. In this model (and its DF generalization[26,27]), the magnetization density in small fields is proportional to the paramagnetic density at the Fermi level $\rho(\vec{r},\epsilon_F)$. This density (Fig. 3) shows a decreased magnetization at the surface compared to the bulk. As would be expected from the DOS (Fig. 2), the magnetization density is mainly d-

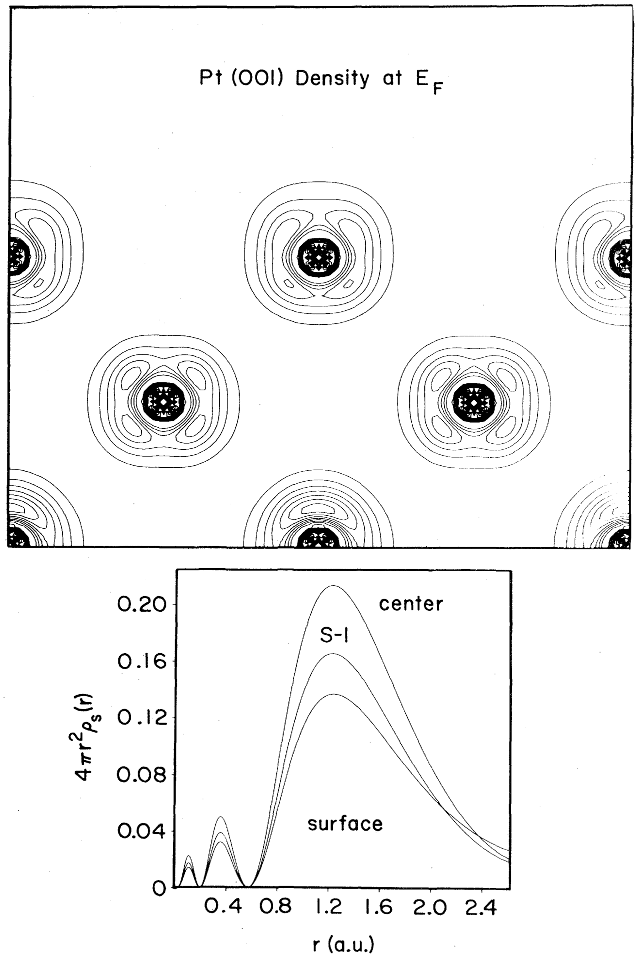

FIG. 3. Paramagnetic density at the Fermi level in a (110) plane and the radial density in the spheres. Total charge is normalized to unity over the film and the contour spacing is 0.002 $e/\text{a.u.}^3$.

like. These results have implications for the hyperfine fields which we now discuss.

The relativistically correct Fermi-contact term, which is generally the largest contribution to the hyperfine energy, is given by[28]

$$\Delta E_{\text{hf}} = -\frac{8\pi}{3} m(\vec{r}=\vec{0})\langle \vec{\mu}_e \cdot \vec{\mu}_N \rangle , \tag{19}$$

where $\vec{\mu}_e$ ($\vec{\mu}_N$) is the magnetic dipole moment of an electron (nucleus) and $m(\vec{r}=\vec{0})$ is the magnetization density at the nucleus. Since the energy of the nuclear moment in an external field $\vec{\text{H}}_{\text{ext}}$ is

$$\Delta E_N = -\vec{\mu}_N \cdot \vec{\text{H}}_{\text{ext}} , \tag{20}$$

it is standard to define a (nonrelativistic) effective hyperfine field strength H_{hf} by

$$H_{\text{hf}} = \frac{8\pi}{3} \mu_B m(\vec{r}=\vec{0}) , \tag{21}$$

where μ_B is the Bohr magneton; with $m(\vec{r}=0)$ given in a.u. H_{hf} is found (in kG) from the conversion 1 a.u. = 524 kG. In general there are two contributions to the contact term for transition metals: (1) The large negative polarization of the core electrons due to the d moment, and (2) a direct polarization of the valence s electrons. From calculations on transition metals it has been found that the core polarization per unpaired spin $H_{\text{hf}}(d)$ is roughly a constant regardless of the local environment.[29] Hence, since there is a decreased magnetization at the surface, there should be a decrease in magnitude of the negative core-polarization field.

The valence contribution in ferromagnetic materials such as Ni and Fe is also negative due to the predominance of the indirect (or covalent) polarization[30] associated with the opposite-sign conduction electrons over the direct (Hund's-rule) coupling to the unpaired d electrons.[29] In a paramagnet such as Pt this contribution will be positive because the direct polarization is clearly the dominant mechanism since the exchange (spin) splitting of the bands is infinitesimal. In the simple Stoner-type picture,[26,27] this term is proportional to the s DOS at the Fermi level (cf. Fig. 2); hence we expect an increase in the valence contribution at the surface. Combining these two effects, we expect that the contact hyperfine field at the surface is more positive than in the bulk. The Knight shift is then related to the hyperfine energy (or nonrelativistically to the hyperfine field) by

$$K = \frac{\Delta E_{\text{hf}}(H_{\text{ext}})}{\Delta E_N(H_{\text{ext}})} = \frac{H_{\text{hf}}}{H_{\text{ext}}} . \tag{22}$$

Hence, we expect that the change in the Knight shift between the bulk and the surface, $\Delta K \equiv K(\text{surface}) - K(\text{bulk})$, is positive. These results then give a quantitative understanding of the NMR results[4,5]; in order to get quantitative results the magnetic field must be included explicitly.

We have carried out self-consistent calculations for a number of external magnetic fields in the range of 0.1–2.0 mRy (1.0 mRy $= 2.35 \times 10^6$ G) using the standard nonrelativistic exchange-correlation potential,[10,21] and have found that even at these high experimental fields, the magnetization scaled approximately with the field. The calculations including relativistic corrections to both the exchange[11,16] and spin density were done in an applied field of 0.1 mRy.

In Fig. 4 we present the self-consistent magnetization density obtained in the presence of an external field. The self-consistent magnetization shows a negative spin density similar to Ni in the region between the atoms, in addition to an increased s-p hybridization compared to the paramagnetic $\rho(\vec{r},E_F)$. The exchange enhancement [which is of the order of 2–3 for bulk Pt (Ref. 18)] manifests itself as a further increase in the difference between the bulk and surface radial magnetization (Fig. 4) compared to the corresponding difference for $\rho(\vec{r},E_F)$ (cf. Fig. 3). These results are essentially the same regardless of whether the relativistic corrections to exchange or the spin density are included since these corrections affect only the region very near the nucleus. For example, in a field of 0.1 mRy, the magnetic moments in all cases are $0.012\mu_B$,

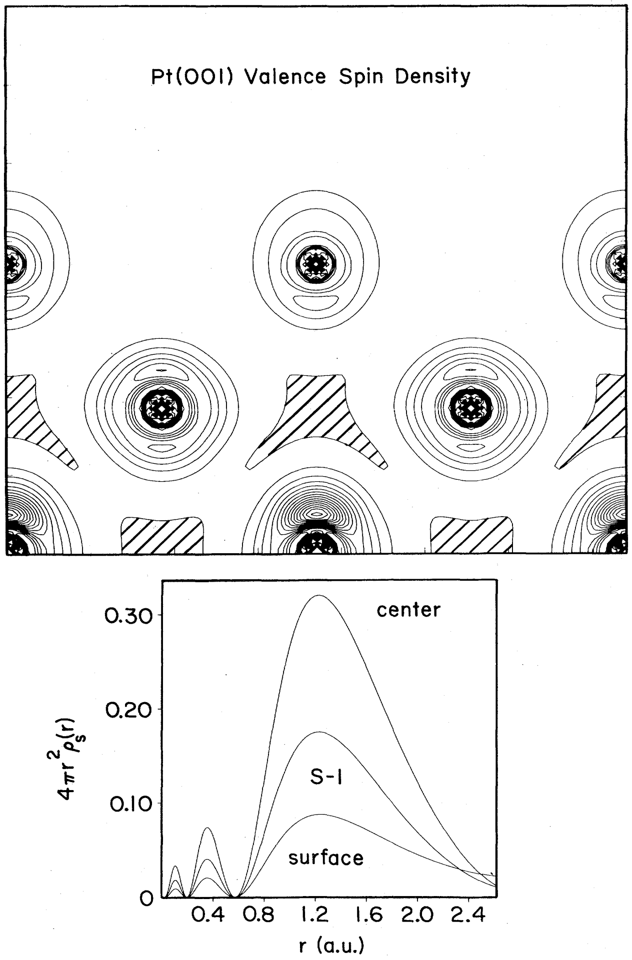

FIG. 4. Self-consistent spin density for Pt(001) in an applied external field of 1.0 mRy. Normalization and contour spacings are as in Fig. 3. Cross-hatched regions in the interstitial denote negative spin densities.

TABLE I. Calculated Knight shift contact contributions (in percent) by layer for a five-layer Pt(001) film. See text for a discussion of the different values. Bulk experimental value is included for reference.

	Central	$S-1$	Surface
Nonrelativistic			
Valence	4.4	4.3	9.5
Core	−16.5	−11.3	−8.5
Total	−12.1	−7.0	1.0
Relativistic exchange			
Valence	4.6	4.4	8.2
Core	−17.0	−11.6	−8.7
Total	−12.4	−7.2	−0.5
Relativistic spin			
Valence	1.3	1.3	2.4
Core	−5.4	−3.9	−3.0
Total	−4.1	−2.6	−0.6
Bulk experiment	−3.4		

$0.008\mu_B$, and $0.006\mu_B$ upon going from the center of the surface of the film.

In Table I we present the calculated (spin-only) Knight shifts for the Pt film. The following three sets of calculated values are given. (a) "Nonrelativistic" uses the standard nonrelativistic prescription for obtaining the magnetization as discussed above and the standard exchange-correlation potential.[10,21] The hyperfine field is obtained via Eq. (21) and the Knight shift is then obtained from the field form of Eq. (22). (b) "Relativistic exchange" values are obtained exactly as the nonrelativistic ones, except that the relativistic correction to exchange[11,16] was included. (c) Finally, the "relativistic spin" values are obtained by including relativistic corrections to the fields and spin density. As discussed in the preceding section we make a local relativistic correction to the magnetization density. For relativistic electrons, we cannot obtain the Knight shift as in cases (a) and (b) above, but rather we must use the energy form of Eq. (22) because of the relativistic transformations of the electromagnetic fields. Within the nonrelativistic spin-only viewpoint adopted for the fields, the average effective external magnetic field $\tilde{H}_{\text{ext}}$ seen by a single relativistic electron is reduced by a factor of $\xi(\zeta=1)$ [cf. Eq. (18)] from the applied field H_{ext}. It is the field $\tilde{H}_{\text{ext}}$, not H_{ext}, that will enter the self-consistent calculation of the charge and spin densities; an analogous reduction of the nuclear dipole field enters into the calculation of ΔE_{hf} as given by Eq. (19). These two competing magnetic field corrections to the Knight shift have the effect of (i) making the self-consistent magnetization density more negative near the nucleus, implying a *negative* contribution to K, and (ii) reducing the magnitude of ΔE_{hf} (and hence K), which for transition metals is equivalent to a *positive* contribution to K.

The first point to notice about the calculated Knight shifts is that the general trends expected from the Stoner-type model are borne out by the spin-polarized calculations: The core-polarization term decreases in magnitude in the surface layers, while the positive valence contribution increases, resulting in a surface Knight shift that is positive with respect to the bulk. The nonrelativistic calculations predict a positive K at the surface and values that are ∼3—4 times larger than experiment. The inclusion of relativistic exchange, which has the effect of reducing the attractive exchange interaction near the nucleus, gives values close to the nonrelativistic results, except that now the competition between the negative core contributions and the positive valence term yields a (small) negative value of K at the surface. It should be noted that while volume-integrated quantities of the charge and spin densities are rather insensitive to the inclusion of relativistic exchange, the radial behavior of the wave functions (especially of the core) is altered. Although the changes in peak positions and heights of each core wave function are slight, the net effect of the large number of electrons in the core can be significant. For example, the output paramagnetic charge density obtained from the potential calculated using the relativistic exchange potential and the self-consistent nonrelativistic density had charge transfers on the order of an electron between the muffin-tin spheres and the interstitial region; the final self-consistent density, however, was quite similar to the nonrelativistic one.

The calculated values of the Knight shift including the relativistic corrections to the magnetization density and fields have the same general trends as the other two sets of results (and experiment), but are quite different numerically. We see that all of the individual contributions are decreased in magnitude, as are the total for the center and subsurface layers. If we add the experimental estimate for the orbital contribution of[31,32] $+0.4\%$ to our spin-only result of -4.1%, we obtain a "bulk" Knight shift of -3.7%, in very good agreement with the experimental value of -3.4%. In contrast, K at the surface is approximately zero when the positive orbital and dipolar contributions at the surface are added to our spin-only results. As stated earlier, the core-polarization field per unpaired spin $H_{\mathrm{hf}}(d)$ is approximately constant for different local environments. From an analysis of the experimental data, Clogston *et al.*[31] and Shaham *et al.*[32] have deduced a value of 1.2×10^6 G for the core polarization per unpaired spin; our calculated value is 1.1×10^6 G. Hence we see that the relativistic corrections to the magnetization density are necessary in order to obtain results in quantitative agreement with experiment for Pt.

V. DISCUSSION AND CONCLUSIONS

From our theoretical results we clearly see that the shifts in the peak of the ^{195}Pt NMR line found in experiment[4,5] is due to (1) a decreased magnetization at the surface compared to the bulk resulting in a decrease in the magnitude of the negative core-polarization contribution, and (2) an increase in the positive valence contribution. For Pt, both of these effects make ΔK positive. For other metals, in particular ferromagnets, we would expect the core and valence contributions to compete. For clean Ni and Fe ferromagnetic surfaces, calculations give an increased magnetization at the surface,[33–35] implying a large negative core contribution; the valence contribution, however, is more positive at the surface.[33–35] We expect that in general the surface valence contribution will be positive with respect to that of the bulk. In bulk transition metals the spatial and symmetry requirements imposed by the structure of the unit cell on the electrons limit the energetically allowed response to the *s-p* electrons to the effective field; i.e., the low-density *s-p* electrons roughly follow the behavior of the high-density d electrons through, for example, hybridization. At the surface, however, the relaxation of these restrictions on the spatial distribution and symmetry of the *s-p* wave functions allows added freedom to respond directly to the effective field. Likewise, a relative increase in the *s-p* hybridization with the surface d DOS, will increase the direct response. The increased direct response of the *s-p* electrons at the surface to the effective (exchange) field will cause the surface valence contribution to ΔK to be positive.

This effect of the surface versus bulk is dramatically demonstrated in calculations on clean[35] and Ag-covered[36] Fe(001) surfaces. At the clean Fe surface the surface valence contribution is positive, while in all subsurface and bulk layers this contribution to the hyperfine field is negative.[36] When an ordered overlayer of Ag is adsorbed,[36] thereby partially reimposing the spatial and symmetry restrictions, the valence contribution changes size and returns to a typical subsurface value. This positive valence contribution to the hyperfine field of the surface relative to bulk appears to be a common feature of all the (magnetic) transition-metal surfaces theoretically studied so far.

Returning to the experimental results,[4,5] we recall that for the clean particles there is a peak in the NMR spectra corresponding to a Knight shift of ~0, which again is quite well reproduced in our calculation. When gases were adsorbed on the surface, new peaks with $K>0$ were seen, suggesting that the surface Pt electrons are all tied up in chemical bonds.[5] (The Knight shifts of typical diamagnetic compounds vary from 0 to 1%.) This explanation[5] is quite plausible, but the data may also be consistent with the less severe requirement that the adsorption of gas molecules at the surface further reduces the magnetization density while still allowing some metallic behavior at the surface. This reduction at the surface would further reduce the core contribution, hence yielding an added positive shift in the NMR spectra. (Although there will be a small relative decrease in the positive valence contribution, this reduction should be much less than for transition-metal adsorption.) Hence it is possible to have both metallic behavior and a near-zero Knight shift at the surface resulting from a cancellation of core and valence contributions. In principle, it is possible to distinguish between zero and nonzero contributions to the total (zero) Knight shift by considering the Korringa relationship[37] between the spin-relaxation time T_1 and the sum of squares of the individual contributions to K. The T_1 data[3] are clearly in disagreement with zero contributions at the surface,[3] and further support our suggestion that the individual contributions are nonzero.

In summary, we have presented a practical method for including spin and magnetic fields into a scalar relativistic treatment. The spin and external fields (treated as given classical objects) have local relativistic corrections obtained from results on the homogeneous electron gas. These corrections, which act only very near to the nucleus, are important for properties such as hyperfine fields and Knight shifts. In the formulation we have given, there is a natural evolution from the familiar nonrelativistic spin-polarized theory to the (spin-only) fully relativistic result, thereby making the conceptional transition between the two limits quite easy.

In our application to the problem of the Knight shift of small Pt particles, we find that the relativistic corrections to the spin and fields are necessary in order to obtain quantitative agreement with experiment. Our results show that the Knight shift of the surface is positive compared to the bulk due to a decreased magnetization at the surface and an increased positive valence contribution. These results are in good quantitative agreement with recent NMR experiments[4,5] on small Pt particles and demonstrate that even spin-related problems for heavy materials such as Pt can be attacked within the local-density framework as outlined here.

ACKNOWLEDGMENTS

We would like to thank W. P. Halperin and D. S. Wang for discussions. This work was supported in part by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC02-76CH00016 and by the National Science Foundation under grant No. DMR-82-16543.

---

[1] I. Yu, A. A. V. Gibson, E. R. Hunt, and W. P. Halperin, Phys. Rev. Lett. 44, 348 (1980).

[2] I. Yu and W. P. Halperin, J. Low Temp. Phys. 45, 189 (1981).

[3] C. P. Slichter, Surf. Sci. 106, 382 (1981).

[4] H. T. Stokes, H. E. Rhodes, P. K. Wang, C. P. Slichter, and J. H. Sinfelt, in *Nuclear and Electron Resonance Spectroscopies Applied to Material Science*, edited by E. M. Kaufmann and G. K. Shenony (North-Holland, New York, 1981), pp. 253–258.

[5] H. E. Rhodes, P. K. Wang, H. T. Stokes, C. P. Slichter, and J. H. Sinfelt, Phys. Rev. B 26, 3559 (1982).

[6] H. E. Rhodes, P. K. Wang, C. D. Makowka, S. L. Rudaz, H. T. Stokes, C. P. Slichter, and J. H. Sinfelt, Phys. Rev. B 26, 3569 (1982); H. T. Stokes, H. E. Rhodes, P. K. Wang, C. P. Slichter, and J. H. Sinfelt, *ibid.* 26, 3575 (1982).

[7] G. C. Carter, L. H. Bennett, and D. J. Kahan, Prog. Mater. Sci. 20, 295 (1977).

[8] See, e.g., C. P. Slichter, *Principles of Magnetic Resonance*, 2nd ed. (Springer, New York, 1980).

[9] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, *ibid.* 140, A1133 (1965).

[10] U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).

[11] A. H. MacDonald and S. H. Vosko, J. Phys. C 12, 2977 (1979).

[12] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B 24, 864 (1981); M. Weinert, J. Math. Phys. 22, 2433 (1981).

[13] Preliminary results using the standard approach were given in D. S. Wang, A. J. Freeman, and M. Weinert, J. Magn. Magn. Mater. 31-34, 891 (1983).

[14] J. D. Bjorken and S. D. Drell, *Relativistic Quantum Mechanics* (McGraw-Hill, New York, 1964); *Relativistic Quantum Fields* (McGraw-Hill, New York, 1965).

[15] A. K. Rajagopal and J. Callaway, Phys. Rev. B 7, 1912 (1973).

[16] A. K. Rajagopal, J. Phys. C 11, L943 (1978).

[17] G. Baym, *Lectures on Quantum Mechanics* (Benjamin, New York, 1976), pp. 558–563.

[18] A. H. MacDonald, J. M. Daams, S. M. Vosko, and D. D. Koelling, Phys. Rev. B 23, 6377 (1981).

[19] D. D. Koelling and B. N. Harmon, J. Phys. C 10, 3107 (1977); T. Takeda, Z. Phys. B 32, 43 (1978); H. Gollisch and L. Fritsche, Phys. Status Solidi B 86, 145 (1978).

[20] M. V. Ramana and A. K. Rajagopal, J. Phys. C 12, L845 (1979).

[21] L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[22] C. S. Wang and A. J. Freeman, Phys. Rev. B 19, 793 (1979).

[23] B. E. Nieuwenhuys and W. H. M. Sachlter, Surf. Sci. 34, 317 (1973).

[24] D. E. Eastman, Phys. Rev. B 2, 1 (1970); P. E. C. Franken and V. Ponec, Surf. Sci. 53, 341 (1975); R. Kh. Burshtein, N. A. Shurmovskaya, T. V. Kalish, and L. A. Larin, Electrokhimiya 13, 799 (1977) [Sov. Electrochem. 13, 677 (1977)].

[25] S. Hagström, H. B. Lyon, and G. A. Somorjai, Phys. Rev. Lett. 15, 491 (1965); H. B. Lyon and G. A. Somorjai, J. Chem. Phys. 46, 2539 (1967).

[26] S. H. Vosko and J. P. Perdew, Can. J. Phys. 53, 1385 (1975).

[27] O. Gunnarsson, J. Phys. F 6, 587 (1976).

[28] E. Fermi, Z. Phys. 60, 320 (1930).

[29] A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1964), Vol. II A, p. 167.

[30] P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. 6, 124 (1961); A. M. Clogston and P. W. Anderson, *ibid.* 6, 124 (1961).

[31] A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. 134, A650 (1964).

[32] M. Shaham, U. El-Hanany, and D. Zamir, Phys. Rev. B 17, 3513 (1978).

[33] O. Jepson, J. Madsen, and O. K. Andersen, Phys. Rev. B 26, 2790 (1982).

[34] A. J. Freeman, E. Wimmer, and H. Krakauer, Bull. Am. Phys. Soc. 28, 298 (1983).

[35] S. Ohnishi, A. J. Freeman, and M. Weinert, J. Magn. Magn. Mater. 31-34, 889 (1983).

[36] S. Ohnishi, A. J. Freeman, and M. Weinert, Bull. Am. Phys. Soc. 28, 297 (1983).

[37] J. Korringa, Physica (Utrecht) 16, 601 (1950); Y. Obata, J. Phys. Soc. Jpn. 18, 1020 (1963); Y. Yafet and V. Jaccarino, Phys. Rev. 133, A1630 (1964).